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(54) Title: A MATERIAL FOR STRUCTURAL COMPONENTS OF AN ELECTROWINNING CELL FOR PRODUCTION OF METAL



(57) Abstract: A material suitable for use for structural components in a cell for the electrolytic reduction of alumina to aluminium metal defined either by: • the formula  $(A'_{1-u}A''_u)_x(B'_{1-v}B''_v)_y(C'_{1-w}C''_w)_zO_4$ , in which A' and A'' are divalent elements from the group Co, Ni, or Zn, B' and B'' are trivalent elements from the group Al, Cr, Mn, or Fe, and C' and C'' are the tetravalent elements Ti or Sn. O is the element oxygen.  $0 \leq u < 1$ ,  $0 \leq v < 1$ ,  $0 \leq w < 1$ ,  $1 \leq x \leq 2$ ,  $0 \leq y \leq 2$  and  $0 \leq z \leq 1$ ,  $x+y+z = 3$  and  $2x+3y+4z = 8$ , or • the formula  $A'_{1-s}A''_sTiO_3$ , in which A' and A'' are divalent elements from the group Co, Ni, or Zn. O is the element oxygen.  $0 \leq s < 1$  or • the formula  $A'_{1-t}A''_tO$ , in which A' and A'' are divalent elements from the group Co, Ni, or Zn. O is the element oxygen.  $0 \leq t < 1$ .

which A' and A'' are divalent elements from the group Co, Ni, or Zn. O is the element oxygen.  $0 \leq t < 1$ .

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**A material for structural components of an electrowinning cell for production of metal**

**Field of Invention**

The present invention relates to a material that can be used for structural components in a cell for the electrolysis of alumina dissolved in a fluoride containing molten salt bath by the use of essentially inert electrodes.

**Background Art**

Conventionally, aluminium is produced by the electrolysis of alumina dissolved in a cryolite based molten salt bath by the more than hundred years old Hall-Heroult process. In this process carbon electrodes are used, where the carbon anode is taking part in the cell reaction resulting in the simultaneous production of CO<sub>2</sub>. The gross consumption of the anode is up to 550 kg/tonne of aluminium produced, causing emissions of greenhouse gases like fluorocarbon compounds in addition to CO<sub>2</sub>. For both cost and environmental reasons the replacement of carbon anodes with an effectively inert material would be highly advantageous. The electrolysis cell would then produce oxygen and aluminium.

An earlier, not yet disclosed Norwegian patent application No. 2001-0927 describes the development and design of a novel electrowinning cell for aluminium production. The novel cell is based on vertical electrode technology and a two chamber electrolysis cell for separation of produced metal and evolved oxygen gas. The cell concept requires that certain structural elements are made of materials that must fulfil their functional requirements at elevated temperatures in an environment of a molten fluoride-based electrolyte. In some regions of the cell an additional requirement is that the materials must fulfil their functional requirements in contact with liquid aluminium, while in other regions the materials must fulfil their functional requirements in contact with pure oxygen gas at a pressure of about one bar.

**Object of the Invention**

The object of the present invention is to identify a material that is stable at an oxygen partial pressure of 1 bar at temperatures above about 680°C and has a sufficiently low solubility in the electrolyte to be used as a material for structural cell components in

oxidizing regions of an aluminium electrowinning cell based on substantially inert electrodes.

## Summary of the Invention

The invention is the conclusion of an extensive search for materials capable of fulfilling the requirements for a material for structural cell components in oxidizing regions of an aluminium electrowinning cell based on substantially inert electrodes. The stability requirements of such a material are similar to those of an inert anode in said electrowinning cell. In the not yet published Norwegian Patent Application No. 2001-0928 the choice of possible element oxides for an inert anode is narrowed to:  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$  and  $\text{HfO}_2$ . The main requirements for a material intended for use in structural cell components are stability at 1 bar oxygen pressure at temperatures above  $680^\circ\text{C}$  and a low solubility in the molten electrolyte. The electrical properties are less important, but its electrical conductivity should be far less than the electrical conductivity of the electrodes and the electrolyte. The material should either itself fulfil the requirements, or it should upon contact with the molten electrolyte react to form a surface layer of an aluminate that fulfils the said requirements. Based on solubility considerations,  $\text{CuO}$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$  are eliminated from the list of possible element oxides, and we are left with:  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SnO}_2$ .

The evaluation leads to three groups of materials:

The first group comprises mixed oxides of the spinel structure with composition  $(\text{A}'_{1-u}\text{A}''_u)_x(\text{B}'_{1-v}\text{B}''_v)_y(\text{C}'_{1-w}\text{C}''_w)_z\text{O}_4$ , in which  $\text{A}'$  and  $\text{A}''$  are divalent elements, *i. e.*, Co, Ni, or Zn,  $\text{B}'$  and  $\text{B}''$  are trivalent elements, *i. e.*, Al, Cr, Mn, or Fe and  $\text{C}'$  and  $\text{C}''$  are tetravalent elements, *i. e.*, Ti or Sn. O is the element oxygen.  $0 \leq u < 1$ ,  $0 \leq v < 1$ ,  $0 \leq w < 1$ ,  $1 \leq x \leq 2$ ,  $0 \leq y \leq 2$  and  $0 \leq z \leq 1$ ,  $x+y+z = 3$  and  $2x+3y+4z = 8$ .

The second group comprises mixed oxides of the ilmenite structure with composition  $\text{A}'_{1-s}\text{A}''_s\text{TiO}_3$ , in which  $\text{A}'$  and  $\text{A}''$  are divalent elements, *i. e.*, Co, Ni, or Zn. O is the element oxygen.  $0 \leq s < 1$ .

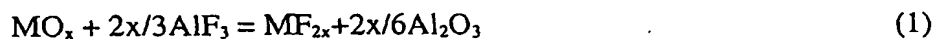
The third group comprises the divalent oxides of Co, Ni and Zn or solid solutions of these. These will react with dissolved alumina to form surface layers of essentially insoluble aluminates. These materials may be expressed by the formula  $A'_{1-t}A''_tO$ ,  $0 \leq t < 1$ .

## Detailed Description of the Invention

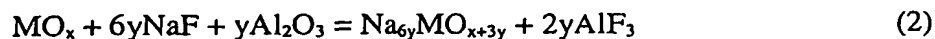
A material suitable as an essentially inert material for structural components in the oxidizing regions of a cell for the electrolytic production of aluminium from alumina dissolved in an essentially fluoride based electrolyte where cryolite is an important ingredient, must be resistant to oxidation and dissolution in the electrolyte. A selection of the element oxides which a material for structural components can consist of, was performed based on the following criteria:

- not a gas or having a high vapour pressure at process temperature

- not converted by cryolite or  $AlF_3$  in the cryolitic mixture, i.e. a large positive value of  $\Delta G^\circ$  for the reaction between the element oxide and  $AlF_3$  to form the element fluoride and aluminium oxide (reaction 1).



- not converted by alumina, i.e. not a negative value of  $\Delta G^\circ$  for the reaction between the element oxide aluminium oxide and sodium fluoride to form a sodium element oxide and aluminium fluoride (reaction 2)



Of elements with the normal valence 2, the only possible elements are thus Co, Ni, Cu and Zn. Of elements with valence 3 one is left with only the elements Cr, Mn, Fe, Ga and Al. Of elements with valence 4 one is left with only the elements Ti, Zr, Hf, Ge and Sn. Cu, Ga, Zr, Hf and Ge may be eliminated from the list based on solubility considerations, and we are left with the following list of elements: Co, Ni, Zn, Al, Cr, Mn, Fe, Ti and Sn. The possible materials for structural cell components in an aluminium electrowinning cell based on substantially inert electrodes are thus limited to the oxides of the listed elements, or combinations of these oxides in mixed oxide compounds.

Under favourable conditions the divalent oxides NiO, CoO and ZnO all react with alumina to form an essentially insoluble surface aluminate layer (reaction 3).



where A = Co, Ni, Zn. Therefore, CoO, NiO and ZnO and solid solutions of these form one group of possible materials for structural cell components. expressed by the formula  $\text{A}'_{1-u}\text{A}''_u\text{O}$ .  $0 \leq u < 1$ . This is further illustrated in Examples 1 and 2.

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Compounds of di- and trivalent element oxides will in this case be of the spinel structure. Spinel like  $\text{NiFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{NiCr}_2\text{O}_4$  and  $\text{CoCr}_2\text{O}_4$  have been suggested and extensively tested as candidates for inert anodes. In these materials, Al from the molten electrolyte has been observed to exchange with the trivalent cation to form essentially insoluble, insulating solid solutions of the type  $\text{Ni}(\text{B}'_{1-v}\text{Al}_v)_2\text{O}_4$ , where  $0 < v < 1$ ,  $\text{B}' = \text{Fe, Cr, Mn}$ . This is further illustrated in Examples 3, 4, and 6. These materials are thus possible materials for structural cell components. The pure aluminates  $\text{NiAl}_2\text{O}_4$ ,  $\text{CoAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  are also possible materials for structural cell components.

15

One compound of di- and tetravalent element oxides,  $\text{Zn}_2\text{SnO}_4$ , forms a spinel oxide. This material may in principle be used for structural cell components.

20

Other stable spinel compositions that are possible materials for structural components of an aluminium electrowinning cell are achieved by substituting a divalent/trivalent spinel with a tetravalent oxide, while simultaneously adjusting the contents of the divalent and trivalent oxides in order to maintain the site and charge balance requirements of the spinel structure. An embodiment of this invention is exemplified in Example 5.

25

Spinel type materials thus form the second group of materials for structural components of aluminium electrowinning cells. The possible spinels according to the present invention are given by the formula  $(\text{A}'_{1-u}\text{A}''_u)_x(\text{B}'_{1-v}\text{B}''_v)_y(\text{C}'_{1-w}\text{C}''_w)_z\text{O}_4$ , in which A' and A'' are divalent elements, *i. e.*, Co, Ni, or Zn, B' and B'' are trivalent elements, *i. e.*, Al, Cr, Mn, or Fe, and C' and C'' are tetravalent elements, *i. e.*, Ti or Sn.  $0 \leq u < 1$ ,  $0 \leq v < 1$ ,  $0 \leq w < 1$ ,  $1 \leq x \leq 2$ ,  $0 \leq y \leq 2$  and  $0 \leq z \leq 1$ ,  $x+y+z = 3$  and  $2x+3y+4z = 8$ .

30

Another group of materials for structural components of aluminium electrowinning cells comprise the ilmenite type materials,  $\text{NiTiO}_3$ ,  $\text{CoTiO}_3$  and solid solutions of these. These compositions are given by the formula  $\text{A}'_{1-s}\text{A}''_s\text{TiO}_3$ , in which A' and A'' are divalent elements, *i. e.*, Co, Ni, or Zn. O is the element oxygen.  $0 \leq s < 1$ .

The invention shall in the following be further described by figures and examples where:

**Figure 1:** Shows a photograph of a sample of a material for structural components in an electrolysis cell before and after the stability test of Example 3.

**Figure 2:** Shows a backscatter SEM photograph of the reaction zone of a  $\text{Ni}_{1.1}\text{Cr}_2\text{O}_4$  material after 50 hours of exposure to molten fluoride electrolyte under anodic polarization.

**Figure 3:** Shows a backscatter SEM photograph of a  $\text{NiFeCrO}_4$  sample after 50 hours of exposure to molten fluoride electrolyte under anodic polarization.

**Figure 4:** Shows a backscatter SEM photograph of a sample of  $\text{Ni}_{1.5+x}\text{FeTi}_{0.5-x}\text{O}_4$  after the stability test of Example 5.

**Figure 5:** Shows a backscatter SEM photograph of a  $\text{Ni}_{1.01}\text{Fe}_2\text{O}_4$  sample after 30 hours of exposure to molten fluoride electrolyte under anodic polarization.

#### **Example 1:**

**Test of the stability of a NiO sample anodically polarized in a molten fluoride electrolyte.**

A cermet with 75 wt% NiO and 25 wt% Ni was prepared using INCO Ni powder type 210, and NiO from Merck, Darmstadt. The material was sintered in argon atmosphere at 1400°C for 30 min.

The sample was exposed to a molten fluoride bath under anodic polarization in order to ensure a partial pressure of 1 bar oxygen on the sample surface. The electrolyte was contained in an alumina crucible with inner diameter 80 mm and height 150 mm. An outer alumina container with height 200 mm was used for safety, and the cell was covered with a lid made from high alumina cement. In the bottom of the crucible a 5 mm thick  $\text{TiB}_2$  disc was placed, which made the liquid aluminium cathode stay horizontal. The electrical connection to the cathode was provided by a  $\text{TiB}_2$  rod supported by an alumina tube to avoid oxidation. A platinum wire provided electrical connection to the  $\text{TiB}_2$  cathode rod. A Ni wire provided for the electrical connection to the anode. The Ni wire and the anode above the electrolyte bath was masked with an alumina tube and alumina cement to prevent oxidation.

340 g Al, (99.9% pure), from Hydro Aluminium was placed on the TiB<sub>2</sub> disc at the bottom of the alumina crucible.

5 The electrolyte was made by adding to the alumina crucible a mixture of :

532 g Na<sub>3</sub>AlF<sub>6</sub> (Greenland cryolite)

105 g AlF<sub>3</sub> (from Norzink, with about 10 % Al<sub>2</sub>O<sub>3</sub> )

35 g Al<sub>2</sub>O<sub>3</sub> (annealed at 1200°C for some hours)

21 g CaF<sub>2</sub> (Fluka p.a.)

10 The sample of the material for structural cell components was suspended above the electrolyte during heating of the cell. The temperature was maintained at 970°C during the whole experiment. The sample of the material for structural cell components was lowered into the molten electrolyte and polarized anodically with a current density of  
15 750 mA/cm<sup>2</sup> based on the bottom end cross sectional area of the sample. The real current density was somewhat lower because the side surfaces of the anode were also dipped into in the electrolyte.

20 The experiment lasted for 8 hours. XRD (X-ray diffraction) analysis of the anode after the experiment showed that the Ni metal was oxidized to NiO and the anode material was covered by an dense, protective, insulating layer of NiAl<sub>2</sub>O<sub>4</sub>.

#### Example 2:

25 **Test of the stability of a ZnO sample anodically polarized in a molten fluoride electrolyte.**

ZnO was doped with 0.5 mol% AlO<sub>1.5</sub>. Two Pt wires were pressed into the material in the longitudinal axis of the ZnO anode and acted as electrical conductors. The material was sintered at 1300°C for 1 hour.

30 The stability test was performed in the same manner as described in Example 1. The amounts of electrolyte and aluminium were the same. The temperature was 970°C. The current density was set to 1000 mA/cm<sup>2</sup> based on the bottom end cross sectional area of the sample The electrolysis experiment lasted for 24 hours. XRD (X-ray diffraction)

analysis of the sample after the electrolysis experiment showed that ZnO had been converted to  $\text{ZnAl}_2\text{O}_4$  during electrolysis.

**Example 3:**

5      **Test of the stability of a  $\text{Ni}_{1+x}\text{Cr}_2\text{O}_4$  sample anodically polarized in a molten fluoride electrolyte.**

The starting powder was prepared by a soft chemistry route. The appropriate amounts of  $\text{Ni}(\text{NO}_3)_2$ , and  $\text{Cr}(\text{NO}_3)_3$  were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at  $900^\circ\text{C}$  for 10  
10      hours. The sample was cold isostatically pressed at 200 MPa, then sintered at  $1440^\circ\text{C}$  for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 1, but a platinum wire provided electrical connection to the sample. The platinum wire to the  
15      sample was protected by a 5 mm alumina tube. When the electrolysis started the anode was dipped approximately 1 cm into the electrolyte. A photograph of the sample before and after electrolysis is shown in Figure 1.

20      The electrolyte, temperature and current density were the same as described in Example 2.

The stability test lasted for 50 hours. After the experiment the sample was cut, polished and examined in SEM (Scanning Electron Microscope). A reaction zone could be seen between the  $\text{Ni}_{1.1}\text{Cr}_2\text{O}_4$  - material and the electrolyte. Figure 2 shows the backscatter  
25      SEM photograph of the reaction zone. On the photograph one can see a reaction zone that has propagated along the grain boundaries of the  $\text{Ni}_{1.1}\text{Cr}_2\text{O}_4$  material. The white particles are NiO.

30      In the table below the relative EDS analysis results are reported. Ni, Cr, Al, and O were the only elements detected. The aluminium present in the interior of the grains might be due to the preparation of the sample for analysis.

Relative comparison between the elements Ni, Cr and Al:



Element:	Atom % in the centre of the grains in Figure 2:	Atom % in the reaction zone in grain boundaries in Figure 2:
Ni	33	47
Cr	66	8
Al	1	45

The SEM analysis shows that the reaction product consisted of a material where the chromium atoms were partly exchanged with aluminium atoms as described by the formula  $\text{NiCr}_{2-x}\text{Al}_x\text{O}_4$  where x varies from 0 to 2. The reaction product forms an insulating coating.

#### Example 4:

**Test of the stability of a  $\text{NiFeCrO}_4$  sample anodically polarized in a molten fluoride electrolyte.**

The starting powder was prepared by a soft chemistry route. The appropriate amounts of  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Cr}(\text{NO}_3)_3$  were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at  $900^\circ\text{C}$  for 10 hours. The sample was cold isostatically pressed at 200 MPa, then sintered at  $1600^\circ\text{C}$  for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 3. The amounts of electrolyte and aluminium were the same. The current density was set to  $1000 \text{ mA/cm}^2$  based on the cross sectional area of the rectangular sample. The experiment lasted for 50 hours. Examination of the sample after exposure to molten fluorides under anodic polarization showed a several micron thick reaction layer where Cr in the material was partly exchanged with Al atoms. A backscatter SEM photograph of the reaction layer is shown in Figure 3. Light grey areas consist of original  $\text{NiFeCrO}_4$  material. Medium grey area contains almost no Cr atoms and a much lower content of Fe.

EDS analysis of the medium grey reaction layer shown in Fig. 3 compared to original  $\text{NiFeCrO}_4$  material and the inner of the anode light grey area also shown in Fig. 3 are summarized in table below. The only elements detected were Ni, Cr, Fe, Al and O.

Comparison of the relative amounts of Cr, Fe, Ni and Al:

Element:	Atom % in the original $\text{NiFeCrO}_4$ material. Light grey area in Fig. 3.	Atom % in the reaction layer after the test. Medium grey area in Fig. 3.
Cr	33.3	0
Fe	33.3	16
Ni	33.3	35
Al	0	49

The conclusion of the stability test is that the  $\text{NiFeCrO}_4$  material reacts with alumina in the electrolyte and forms a dense, essentially insoluble, insulating layer of  $\text{NiFe}_{1-x}\text{Al}_{1+x}\text{O}_4$ .

#### Example 5:

**Test of the stability of a  $\text{Ni}_{1.5+x}\text{FeTi}_{0.5-x}\text{O}_4$  sample anodically polarized in a molten fluoride electrolyte.**

The starting powder was prepared by a soft chemistry route. The appropriate amounts of  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$  and  $\text{TiO}_5\text{H}_{14}\text{C}_{10}$  (titanyl acetylacetonate) were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at  $900^\circ\text{C}$  for 10 hours. The sample was cold isostatically pressed at 200 MPa, then sintered at  $1500^\circ\text{C}$  for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 3. The amounts of electrolyte and aluminium were the same. The current density was set to  $1000 \text{ mA/cm}^2$  based on the cross sectional area of the rectangular sample. The experiment lasted for 30 hours. After the experiment the sample was cut, polished and examined in SEM. The backscatter photo in Fig. 4 shows the end of the sample facing the cathode. In this experiment no reaction layer was detected on the  $\text{Ni}_{1.5+x}\text{FeTi}_{0.5-x}\text{O}_4$  anode after 30 hours.

#### Example 6:

**Test of the stability of a  $\text{Ni}_{1.01}\text{Fe}_2\text{O}_4$  sample anodically polarized in a molten fluoride electrolyte.**

The starting powder was prepared by a soft chemistry route. The appropriate amounts of  $\text{Ni}(\text{NO}_3)_2$ , and  $\text{Fe}(\text{NO}_3)_3$  were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at  $900^\circ\text{C}$  for 10 hours. The sample was cold isostatically pressed at 200 MPa, then sintered at  $1450^\circ\text{C}$  for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 3. The amounts of electrolyte and aluminium were the same. The current density was set to 1000 mA/cm<sup>2</sup> based on the cross sectional area of the rectangular anode. The experiment was stopped after 30 hours. After the experiment the sample was cut, polished and examined in SEM. Figure 5 shows a backscatter photograph of the sample at the end facing the cathode. An approximately 10 micron thick reaction layer is seen.

A line scan EDS analysis was done to examine whether the layer was a reaction layer or electrolyte adhering to the surface. The line scan indicated a thin layer of bath components, and then a reaction layer of approximately 10 micron thickness. In the interior of the anode and in the reaction layer only oxygen was detected in addition to Ni, Fe and Al. The results are reported in the table below:

Comparison of the relative amounts of Ni, Fe and Al:

Element:	Atom % of element in the interior of the anode shown in Figure 5 and analysed with line scan EDS:	Atom % of element in the reaction layer as shown in Figure 5 and analysed with line scan EDS:
Ni	33	30
Fe	67	30
Al	0	40

In the 10 micron thick reaction layer the iron atoms were partly exchanged with aluminium atoms to form an essentially insoluble, insulating layer of NiFe<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub>.

Claims

1. A material suitable for manufacture of structural components in a cell for electrolytic reduction of alumina to aluminium,

5 characterised by

the formula  $(A'_{1-u}A''_u)_x(B'_{1-v}B''_v)_y(C'_{1-w}C''_w)_zO_4$ , in which A' and A'' are divalent elements from the group Co, Ni, or Zn, B' and B'' are trivalent elements from the group Al, Cr, Mn, or Fe and C' and C'' are the tetravalent elements Ti or Sn, O is the element oxygen,  $0 \leq u < 1$ ,  $0 \leq v < 1$ ,  $0 \leq w < 1$ ,  $1 \leq x \leq 2$ ,  $0 \leq y \leq 2$  and  $0 \leq z \leq 1$ ,  $x+y+z = 3$  and  $2x+3y+4z = 8$ .

10

2. A material suitable for manufacture of structural components in a cell for electrolytic reduction of alumina to aluminium,

characterised by

the formula  $A'_{1-s}A''_sTiO_3$ , in which A' and A'' are divalent elements from the group Co, Ni, or Zn and O is the element oxygen,  $0 \leq s < 1$ .

15

3. A material suitable for manufacture of structural components in a cell for electrolytic reduction of alumina to aluminium,

characterised by

the formula  $A'_{1-t}A''_tO$ , in which A' and A'' are divalent elements from the group Co, Ni, or Zn and O is the element oxygen,  $0 \leq t < 1$ .

20

4. A material in accordance with claim 1,

characterised in that

the cation A' is essentially divalent Ni, u is essentially 0 and x is essentially 1.

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5. A material in accordance with claim 1,

characterised in that

the cation B' is essentially trivalent Al, the cation B'' is essentially trivalent Fe and y is essentially 2.

30

6. A material in accordance with claim 2,

characterised in that

the cation A' is essentially divalent Ni, s is essentially 0, and the cation B' is essentially tetravalent Ti.

7. A material suitable for manufacture of structural components in a cell for electrolytic reduction of alumina to aluminium,

characterised in a first embodiment by

the formula  $(A'_{1-u}A''_u)_x(B'_{1-v}B''_v)_y(C'_{1-w}C''_w)_zO_4$ ,

or in a second embodiment by

the formula  $A'_{1-s}A''_sTiO_3$ ,

or in a third embodiment by

the formula  $A'_{1-t}A''_tO$ ,

in which A' and A'' are divalent elements from the group Co, Ni, or Zn, B' and B'' are trivalent elements from the group Al, Cr, Mn, or Fe and C' and C'' are the tetravalent elements Ti or Sn, O is the element oxygen,  $0 \leq s < 1$ ,  $0 \leq t < 1$ ,  $0 \leq u < 1$ ,  $0 \leq v < 1$ ,  $0 \leq w < 1$ ,  $1 \leq x \leq 2$ ,  $0 \leq y \leq 2$  and  $0 \leq z \leq 1$ ,  $x+y+z = 3$  and  $2x+3y+4z = 8$ .

8. A material in accordance with claim 7,

characterised in that

in the first embodiment of the invention the cation A' is essentially divalent Ni, u is essentially 0 and x is essentially 1.

9. A material in accordance with claim 7,

characterised in that

in the first embodiment of the invention the cation B' is essentially trivalent Al, the cation B'' is essentially trivalent Fe and y is essentially 2.

10. A material in accordance with claim 7,

characterised in that

in the second embodiment of the invention the cation A' is essentially divalent Ni and s is essentially 0.

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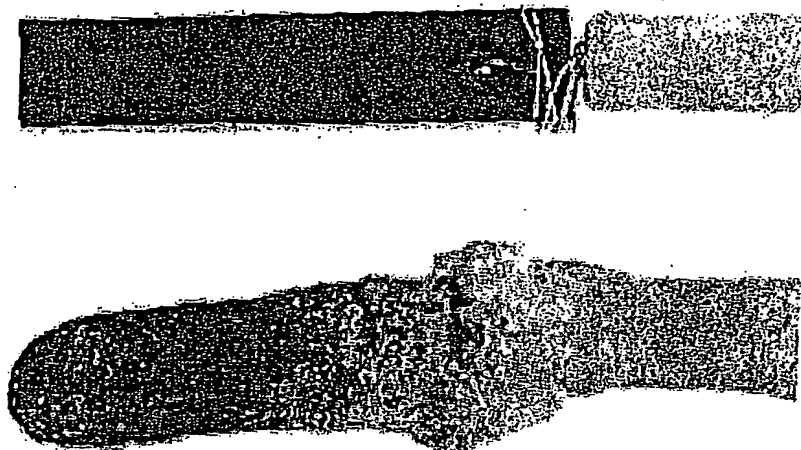


Fig. 1

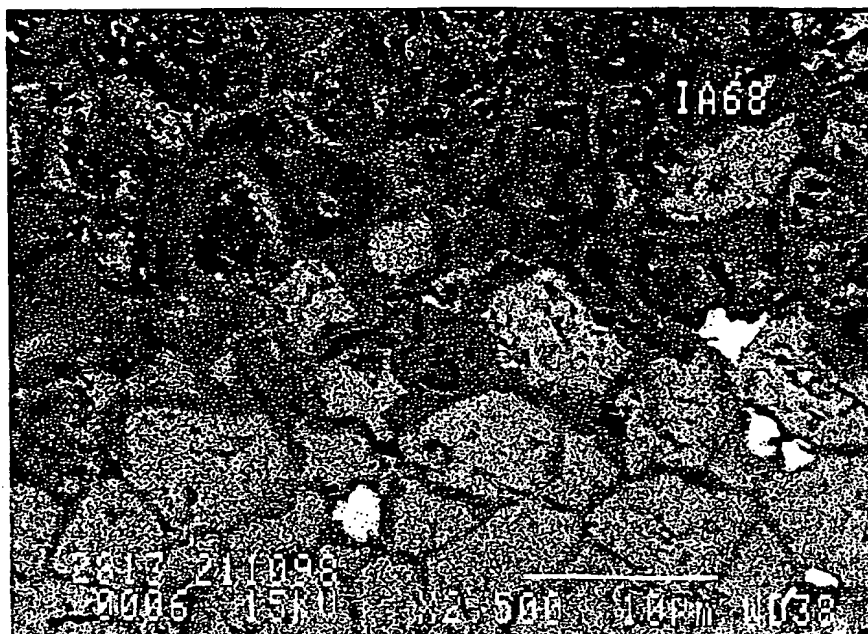


Fig. 2

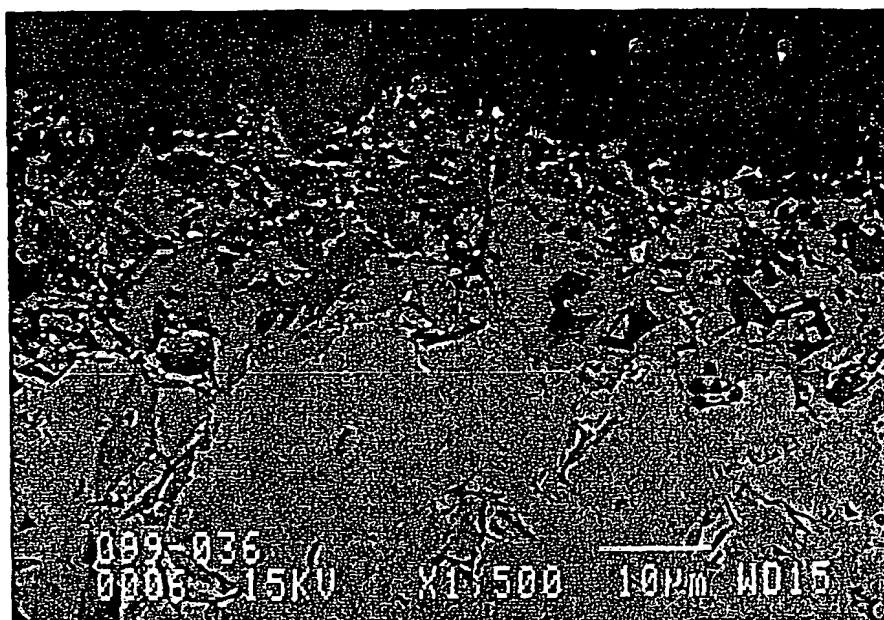


Fig. 3



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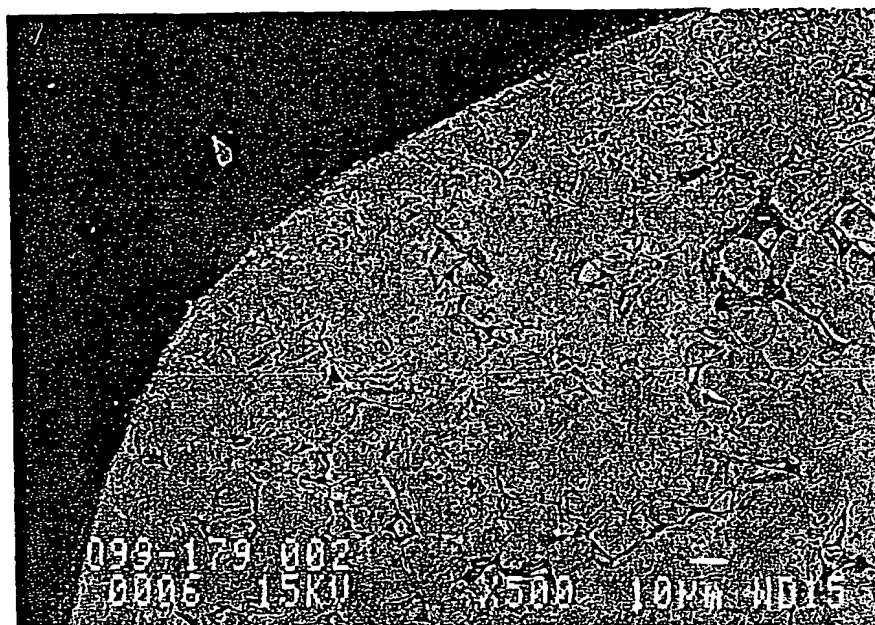


Fig. 4

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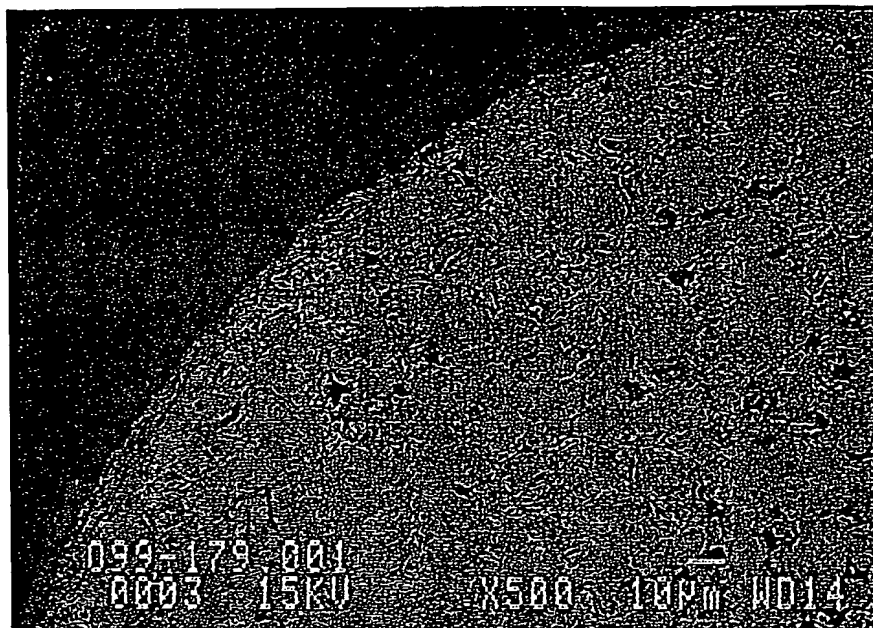


Fig. 5

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NO 2003/000278

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C25C 3/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6423204 B1 (SIBA P. RAY ET AL), 23 July 2002 (23.07.2002), column 1, line 29 - line 32; column 1, line 41 - line 43; column 1, line 53 - line 58, column 2, line 17 - line 32  --	1,4,7,8
A	US 6126799 A (SIBA P. RAY ET AL), 3 October 2000 (03.10.2000), column 1, line 23 - line 50; column 3, line 16 - line 53  --	1-2,4-5,7-10
X,P	WO 02066710 A1 (NORSK HYDRO ASA), 29 August 2002 (29.08.2002), page 3, line 31 - page 4, line 12; page 9 - page 11, line 9  --	1-2,4-5,7-10

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 January 2004

Date of mailing of the international search report

23.01.2004

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 2003/000278

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6113758 A (VITTORIO DE NORA ET AL), 5 Sept 2000 (05.09.2000), column 2, line 24 - line 27; column 3, line 44 - line 52  --	3,7
X	GB 2065708 A (SWISS ALUMINIUM LTD.), 1 July 1981 (01.07.1981), page 1, line 3 - line 21; page 2, line 42 - line 46  -- -----	3,7

# INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/NO03/00278**

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: **6**  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
  
**see next sheet\***
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

**see next sheet\*\***

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/NO03/00278

Box No. IV Text of the abstract (Continuation of item 5 of the first sheet)

★

Independent claim 6 is not drafted in a "clear and concise" manner as is called for in PCT Article 6. The claim describes a cation B' and refers to claim 2. However, a cation B' is not described in claim 2. Consequently, the content of claim 6 does not agree with that of claim 2.

★★

This International Searching Authority found multiple groups of inventions in the international application, as follows:

1. Claims: 1-2, 4-5, 7 (those parts that correspond to claims 1 and 2) and 8-10.

Group 1 describes a material for manufacture of structural components in a cell for electrolytic reduction of alumina to aluminium. The material comprises spinel and ilmenite structures respectively. One component is Ti or Sn.

2. Claims 3, 7 (those parts that correspond to claim 3).

Group 2 describes a material for manufacture of structural components in a cell for electrolytic reduction of alumina to aluminium. The material comprises only divalent oxides and no Ti or Sn.

The "special technical features" in each group of claims are on the whole different from each other. Therefore, these groups of inventions are not so linked together as to form a single inventive concept with regard to PCT Rule 13.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

24/12/2003

International application No.

PCT/NO 2003/000278

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Information on patent family members

24/12/2003

International application No.

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